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ESR STUDY OF IRRADIATED PLASTICS

by

D. ONDERDELINDEN AND L. STRACKEE

(National Institute of Public Health - Bilthoven)

1973

Report prepared by the Radiation Research Laboratory
National Institute of Public Health
Bilthoven - The Netherlands

Euratom contract 033-67-4 PSTN

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ABSTRACT

In connection with a study on the detection of irradiated foodstuffs by means of ESR, the induction of free radicals in plastic packaging material by ionizing radiation was investigated at doses of 2 Mrad. Except for polymers with a large fraction in the glass state above the glass temperature and polymers with plasticizers, radicals can be measured during periods up to a few months. Radical yield was found to depend on dose rate and temperature. A theoretical model that accounts for these parameters is discussed. Decay was found to follow approximately first order kinetics characterized by two rate constants.

KEY WORDS

FREE RADICALS
POLYMERS
PACKAGING
FOOD
IONIZING RADIATIONS
RADIATION DOSIS
TEMPERATURE
IRRADIATION

CONTENTS

ESR STUDY OF IRRADIATED PLASTICS*

1 — INTRODUCTION

It is well known that irradiation of solid material with X-rays, γ-rays and fast electron beams induces the formation of free radicals which can be detected in principle by electron spin resonance (ESR). In the framework of an investigation on identification methods of irradiated foodstuffs, the applicability of this measuring technique was studied. However it appeared from preliminary measurements on foodstuffs [1] that the stability of these radicals is so low that an hour after the irradiation no ESR signal could be measured. This low stability was attributed to the high moisture content. Measurements on dry foodstuffs were more promising indeed. Irradiation of wheat for example gives an approximately 19 gauss broad signal and a radical yield of 3 spins per 100 eV deposited energy. The stability of the resonance signal was low. In a nitrogen atmosphere the half value time was about 40 days. Samples kept in open vessels showed a 4 fold decrease in a few days. Furthermore it may be remarked that in dried foodstuffs a large concentration of radicals was found prior to the irradiation. No significant change was found after the irradiation of these samples up to a dose of 1 Mrad. This means that the method can not be used for identification of irradiated foodstuffs as such.

More promising seems an indirect method via the radicals formed in the packaging material that generally encloses the product during the irradiation. Therefore an investigation on the formation and decay of radicals in a number of plastics was started. In this report the results of this investigation are communicated.

2 — EXPERIMENTAL REMARKS

2.1 — Irradiation of the samples, kept in evacuated quartz tubes, were performed with the aid of a 850 Ci Co^{60}-source†. The absorbed dose was calculated from the irradiation time and the estimated exposure rate at the position of the sample, assuming a quadratic dependence of the exposure rate and the distance to the source. The electron density of the sample material was calculated from the Z-values based on the chemical formulae and the specific density. Since there was no need for a determination of the absolute radical yield to a very high precision, at this stage of our work, no attempts were made to apply any correction to the dose thus estimated. The most important sources of error are:

a) deviations from the assumed quadratic relationship;
b) neglect of the radiation scattered from the source holder and the walls of the irradiation well;
c) lack of electron equilibrium due to the small dimensions of the sample.

The accuracy of the dose is estimated to be better than 15%. The dose rate was changed by varying the distance of the samples to the source. The highest dose rate that could be attained was 0.66 Mrad/h and unless stated otherwise it is to be taken that all the samples were irradiated at this dose rate.

* Work performed under Euratom contract 033-67-4 PSTN.
† We wish to acknowledge the Standard Dosimetry Group of our Institute for the use of this source.

2.2 — Resonances were investigated at room temperature with the aid of a home-made spectrometer with the following specifications:

— frequency	:	9000 MHz (X-band)
— sample cavity	:	TE_{102} rectangular (AEG)
— max. microwave power at the sample:		40 mW
— modulation	:	140 kHz by means of a loop outside the cavity
— frequency stabilisation	:	locked to the resonance frequency with a 10 kHz signal applied to the repeller
— klystron	:	Varian type V 153
— magnet	:	Varian type V 3400, 9 inch

The sensitivity of the spectrometer was determined with carbon samples in which the number of free electrons is known. The maximum sensitivity at a time constant of 0.5 sec and a hypothetical line width of 1 gauss is estimated as 10^{12} free spins. Measurements of the spectra were performed at power levels low enough to prevent saturation broadening. The power level mostly used was 2 mW. The modulation amplitude was chosen as 2 gauss, small enough to suppress serious modulation broadening of the spectral lines.

The ESR measurements were performed with the samples in the same tubes in which the samples were irradiated. Due to the formation of colour centres by the irradiation a strong background signal was observed. The colour centres were removed by heating the end of the tube, while the samples were at the other end.

2.3 — The materials studied were obtained from commercial sources and were used without further purification. Most materials were received in form of plates, a few mm thick, and were machined to cylinders of length 5 mm and ∅ 2 mm.

The materials, characterized by some specific properties, are listed below. T_g is the glass temperature, defined as the temperature at which the amorphous glass state changes into the rubber state. ρ means specific density.

1. Polyethene in three varieties:
   a) high-pressure polyethene; a highly branched structure with low crystallinity and high flexibility; $\rho = 0.92$ gram.cm^{-3};
   b) low pressure polyethene; a less branched structure with higher crystallinity and lower flexibility; $\rho = 0.95$ gram.cm^{-3}; molecular weight approximately 800,000;
   c) low pressure polyethene with high molecular weight; approximately 5,000,000 (H.M. polyethene);

   All varieties are non-transparent.
2. Polypropene; highly crystalline isotactic polymer; $\rho = 0.95$ gram.cm^{-3}; $T_g = -15$°C; non-transparent.
3. Polystyrene; amorphous atactic polymer; $\rho = 1.05$ gram.cm^{-3}; $T_g = 100$°C; highly transparent.
4. Polyacetale (polyoxymethene); highly crystalline polymer; $\rho = 1.14$ gram.cm^{-3}; $T_g = -50$°C transparent.
5. Polytetrafluorethene (Teflon); partly amorphous, partly crystalline polymer; $\rho = 2.20$ gram. cm^{-3}; $T_g = 126$°C; transparent,
6. Polycaprolactam (Nylon); crystalline polymer; $\rho = 1.13$ gram.cm^{-3}; $T_g = 50$°C; transparent.
7. Polyvinylchloride; amorphous polymer in three varieties:
   a) PVC-139; $\rho = 1.39$ gram.cm^{-3}; $T_g = 87$°C;
   b) PVC-138; $\rho = 1.35$ gram.cm^{-3}; $T_g = 87$°C;

c) a variety with a high content of plasticizer leading to a glass temperature of about 0°C; $\rho = 1.30$ gram.cm^{-3}.

8. Polymethylmethacrylaat (PMMA); amorphous polymer; $\rho = 1.18$ gram.cm^{-3}; $T_g = 110$°C; an extruded and a cast sample were studied ; both varieties were highly transparent.
9. Phenol-formaldehyde paper (PF-paper); a thermo set polymer; $\rho = 1.40$ gram.cm^{-3}; non-transparent.
10. Phenol-formaldehyde tissue (PF-tissue); a thermo set polymer; $\rho = 1.40$ gram.cm^{-3}; non-transparent.
11. Polycarbonate; amorphous polymer; $\rho = 1.20$ gram.cm^{-3}; $T_g = 150$°C; highly transparent.

All sample tubes were evacuated down to a pressure of about 10^{-5} torr and sealed off. This means that no attempts were made to outgas the samples. A large fraction of gases which might be dissolved in the polymer are still there during the irradiation.

3 — RESULTS

3.1 — Spectra

The spectra, in the derivative form, of the polymers irradiated up to a dose of 2 Mrad at room temperature are given in figures 1, 2 and 3. A spectroscopic splitting value of $g = 2.0013$ is indicated in the figures. This position is determined from the sharp component of the quartz spectrum which according to Weeks[2,3] has a splitting factor of $g = 2.0013 \pm 0.0006$.

Polyethene

In the case of H.M. polyethene a seven line spectrum with a hyperfine splitting (h.f.s.) of 12.5 gauss was found. A similar, but less pronounced, spectrum was found for low pressure low molecular polyethene. No signal was observed for the high pressure polyethene.

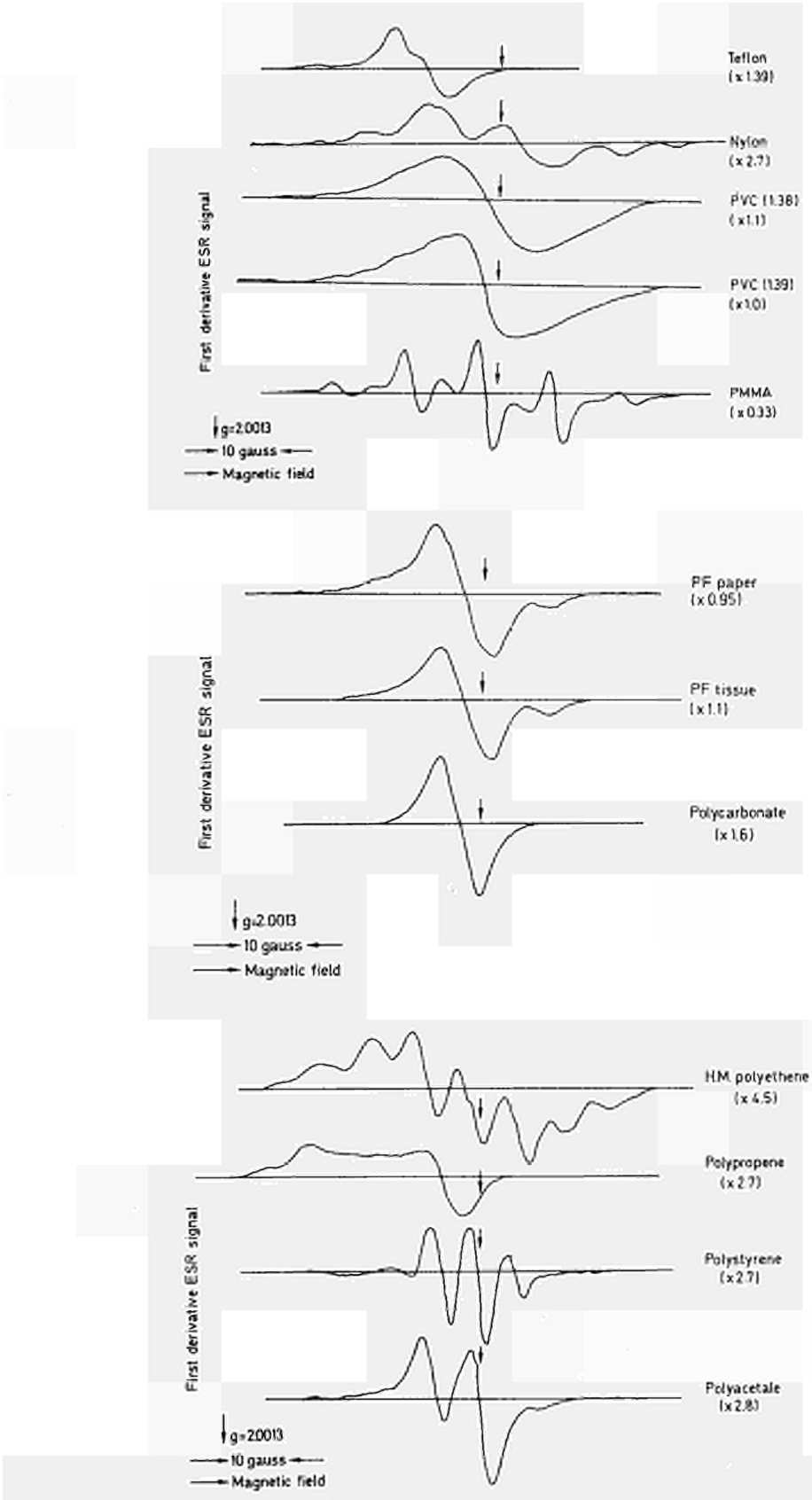
The seven line spectrum might be due to a combination of even and odd spectra with hyperfine splittings in the order of 25 gauss. Lawton *et al.*[4] for instance found after irradiation of high density polyethene a radical, due to hydrogen abstraction from the main chain, giving a 6 line spectrum with a h.f.s. of 31 gauss and furthermore a 5 line spectrum (h.f.s. 20 gauss) which they attributed to main chain scission. Even and odd spectra were also found by Onishi *et al.*[5].

Under the influence of oxygen the spectrum was found to change in an asymmetrical singlet. This radical is probably due to a ROO· radical. The unpaired electron is, according to Abraham and Whiffen[6], strongly localized on the oxygen atom leading to a singlet structure.

Polypropene

In the case of polypropene a spectrum is found which resembles an asymmetric singlet with $g_{//} = 2.033$ and $g_{\perp} = 2.004$. The results are not in accordance with measurements of Onishi *et al.*[5] who found a combination of an eight-line, seven line, six-line and singlet spectra. The observed splittings were all in the order of 20 gauss. A singlet spectrum was found by them after very high irradiation dose (290 Mrad). The form of this spectrum was definitely different from the spectrum presented here.

The most probable explanation for the observed spectrum seems to be the formation of a peroxy-radical, although the asymmetry is rather high.



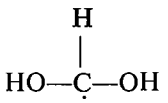
Figs. 1, 2 and 3 — First derivative spectra of polymers measured at room temperature after an irradiation dose of 2 Mrad and a dose rate of 0.66 Mrad/h. The sample tubes were evacuated prior to the irradiation. The spectra as measured with the same sensitivity as the PVC-1.39 spectrum are multiplied with the factor given in the brackets. The sample weight of all samples is about 30 mg so that a rough idea about the radical yield for all polymers can be obtained by comparison with the results of PVC. The arrow indicates a g value of 2.0013 at the same cavity frequency.

Polystyrene

The spectrum of irradiated polystyrene is a triplet, with a h.f.s. of 11 gauss and rather broad lines. This result is in accordance with other work[6,7,8,9]. The radical is of the cyclohexadienyl type and is the result of hydrogen addition to the aromatic ring[10].

Polyacetale

For this polymer a doublet is found with a splitting of 12.5 gauss and lines of 6.5 broad. The main chain of this polymer is of the form $-C^{H2}-O-C^{H2}-O-$ and the radical formed by abstraction of a proton is similar to the methanediol radical



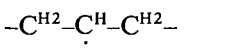
The observed coupling for this radical is 14 gauss. Although the coupling is clearly an α-coupling the splitting is smaller than the expected 23 gauss due to non-planarity at the radical carbon[11, 12,13]. We therefore conclude that the radical observed in polyacetale is formed indeed by hydrogen abstraction from the main chain.

Polytetrafluorethene

For Teflon a spectrum is found that is interpreted as a just resolved doublet with a splitting of 8 gauss and a linewidth of 8 gauss. The g-value is remarkably high: $g = 2.019$. The only spectrum that resembles this spectrum is found by Ard *et al.*[14], where the many line spectrum found directly after irradiation changed after the admission of air in a badly resolved doublet attributed to a $-F^2COO\cdot$ radical. The g-value of this spectrum is close to the free electron value in contradiction to the high g-value of our spectrum.

Polycaprolactam

A badly resolved sextet spectrum is found in Nylon 6. The splitting is about 21 gauss. The radical is probably a radical of the type



The total width of the spectrum is the same as found by Onishi *et al.*[5], although their spectrum seems to be an uneven spectrum.

Polyvinylchloride

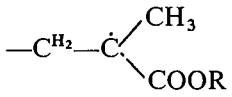
A single gaussian type line is found for the PVC samples without plasticizers. The soft PVC sample did not give a measurable ESR signal. The width ΔH_{pp} between the maxima of the derivative curve is found to differ for the two PVC samples. Values of 20 gauss and 30 gauss were observed. These values were found to depend on irradiation dose and time after the irradiation.

These results are in accordance with work found in the literature[6,15,16]. The spectrum is ascribed by Onishi et al. [17] to a polyenyl radical of the form $-C^{H2}-C^{H}-(CH = CH)_n-C^{H2}-$, stabilized by bond resonances. The ΔH_{pp} value of the singlet decreases when n the number of conjugated bonds increases. The observed widths would correspond to values of n in the range 5 till 10. It may be remarked here that the action of oxygen on very small PVC samples has been

studied by Loy[18]. The change of the ΔH_{pp} value as a function of time can also partly be due to a change of the original radicals to the peroxy form.

Polymethylmethacrylaat

The nine line spectrum of PMMA found originally by Schneider *et al.*[19] has become the subject of considerable discussion. It is now generally agreed that the spectrum is due to one radical. As originally suggested by Abraham *et al.*[20] this radical is of the type



which is produced by chain scission. This radical would have two different configurations and thus the different intensities of the five line set and the four line set would reflect the relative probabilities of the two structures.

PF-paper and PF-tissue

For these thermo sets broad singlets were found with some additional structure which might be a triplet with a splitting of about 20 gauss. The singlet has a width of about 17 gauss for both polymers. The observed structure might be due to a triplet from a radical of the type $\cdot C_{OH}^{H2}$ (splitting - 17.68 gauss) and a singlet of a free electron localized on an oxygen atom. The small value of the α-hydrogen splitting, leading to the triplet, may be attributed to the non planar configuration at the radical carbon.

Polycarbonate

In this nearly completely amorphous polymer a singlet is found with $\Delta H_{pp} = 10.5$ gauss. The spectroscopic splitting factor g is 2.0037. A main chain scission at the carbonate group could give a radical of the type $-O-\dot{C}=O$ which gives a singlet spectrum.

We have however no further indications of this assumption.

3.2 — Free radical yield

The number of spins can be found by double integration of the derivative curve and comparison with a standard sample. In this way we determined the radical yield, i.e. the number of spins per 100 eV dissipated energy. The number of spins per gram as a function of dose and a function of temperature are presented in figures 4 and 5 for high density PVC. The curves are of type

$$N(\infty)\ (1 - \exp - \beta D)$$

with $N(\infty)$ and β constants and D the radiation dose. β is of the order of 0.2 $Mrad^{-1}$. This behaviour is in accordance with results described in the literature[21].

The initial radical yield G is given in the following table:

dose rate	25°C	45°C	60°C
0.11 Mrad/h	5.8	3.8	2.9
0.66 Mrad/h	4.6	3.9	3.5

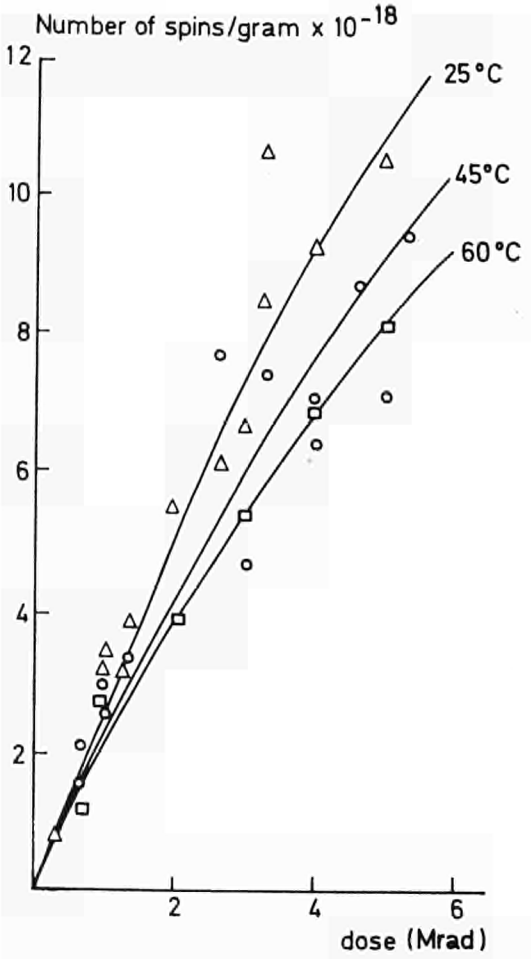


Fig. 4 — The number of spins per gram as measured in PVC-1.39 as a function of irradiation dose at a dose rate of 0.66 Mrad/h. The ESR measurements were performed at room temperature, the irradiations at different temperatures as indicated.

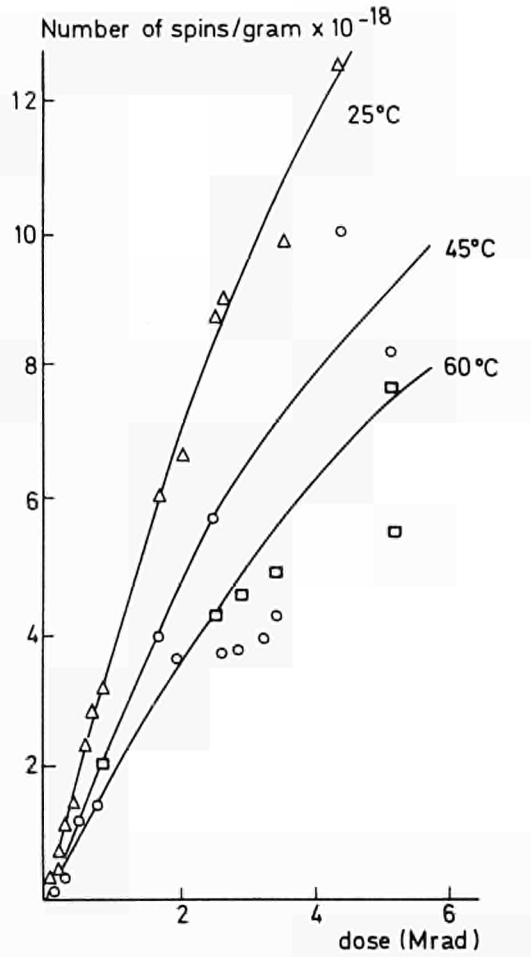


Fig. 5 — As in fig. 4 at a dose rate of 0.11 Mrad/h.

The above mentioned measurements were performed in air. A measurement of a PVC sample in vacuum, outgassed at 80°C, resulted in the same spectrum and about the same radical yield as compared with similar measurements in air.

It can be seen from these measurements that the dose rate as well as the temperature influence the radical yield.

At room temperature a higher dose rate is seen to result in a lower radical yield, while at higher temperature the reversed situation occurs.

To check the dose rate and the spin concentration measurements on L-α-alanine have been performed for different dose rates. The resulting radical yield was found to be 6.0 ± 0.5 spins/100 eV for dose rates of 0.11 Mrad/h, 0.22 Mrad/h and 0.66 Mrad/h with a total dose of 2 Mrad. From measurements of Ebert *et al.*[22] it follows that a dose rate effect does not occur in alanine up to a dose rate of 3 Mrad/h. Furthermore a saturation effect did not show up for a dose of 2 Mrad. The results obtained for alanine for the different dose rates shows that the dose rate effect in PVC is not due to errors in the dose rate. The absolute accuracy of the spin con-

centration is not checked easily. Results of the radical yield of L-α-alanine, obtained by different authors, range from $G = 1.2$ spins/100 eV[22], $G = 2.5$ spins/100 eV[23] to $G = 8.0$ spins/100 eV [24]. In connection with our results on the radical yield in PVC it is interesting to mention the results of Onishi *et al.*[15]. They irradiated this material at -196°C with 2 MeV electrons and determined the concentration of radicals as a function of dose. The initial irradiation yield found was 7.1 spins/100 eV, while the saturation value for the radical concentration was about 1×10^{20} spins/gram.

3.3 — Decay of the radicals

The stability of the radicals in the irradiated polymers is shown in figures 6,7,8 and 9. In these figures the amplitude of the ESR signal is plotted logarithmically versus time. For most radicals two runs were made, one with the sample in vacuum and the other in air. In most cases the decay seems to be governed by first order kinetics with two decay times. The short time decay is in the order of a few days and the long time decay a factor 10 higher. The difference for decay in air and in vacuum is generally not large, only for H.M. polyethene a decrease in signal versus time is found in vacuum and an increase in signal vs. time in air. As mentioned earlier this should be due to the formation of the ROȮ radical which would have in that case a higher amplitude than the original radical.

Temperature dependent decay was measured for PVC. PVC samples were irradiated up to a dose of 3.6 Mrad at a dose rate of 0.11 Mrad/h and the decay was followed at 80°C and at 30°C, both in a vacuum of about 10^{-3} torr. For both cases two decay times (half value times) were found:

80°C	$t^{(1)}_{\frac{1}{2}} = 6.6$ min	$t^{(2)}_{\frac{1}{2}} = 180$ min
30°C	$t^{(1)}_{\frac{1}{2}} = 0.5$ days	$t^{(2)}_{\frac{1}{2}} = 60$ days

From these results an activation energy of 45 kcal/mole and a pre-exponential factor 1.4×10^{12} sec^{-1} was calculated for the slow decay. For the fast decay corresponding values are 35 kcal/mole and $6.7 \times 10^{9} sec^{-1}$.

4 — THEORETICAL CONSIDERATIONS — DISCUSSION OF THE RESULTS

At low doses the number of radicals induced by radiation is proportional to the observed energy. At higher doses in most irradiated plastics a saturation effect is seen to occur. In this study such an effect was also observed in irradiated PVC. The saturation of the number of induced spins can be described by an exponential equation

$$N(D) = N(\infty)\,(1 - \exp - \beta D)$$

where $N(D)$ is the number of radicals;
$N(\infty)$ the saturation value and
β a constant.

The exponential behaviour can be understood if it is assumed that the radicals formed previously can be destroyed by irradiation. In a detailed study of the kinetics involved in the production of radicals in alanine single crystals Snipes and Horan[25] have demonstrated this process clearly. They found that radicals of a different type than those induced by ionizing radiation and as such

Fig. 6

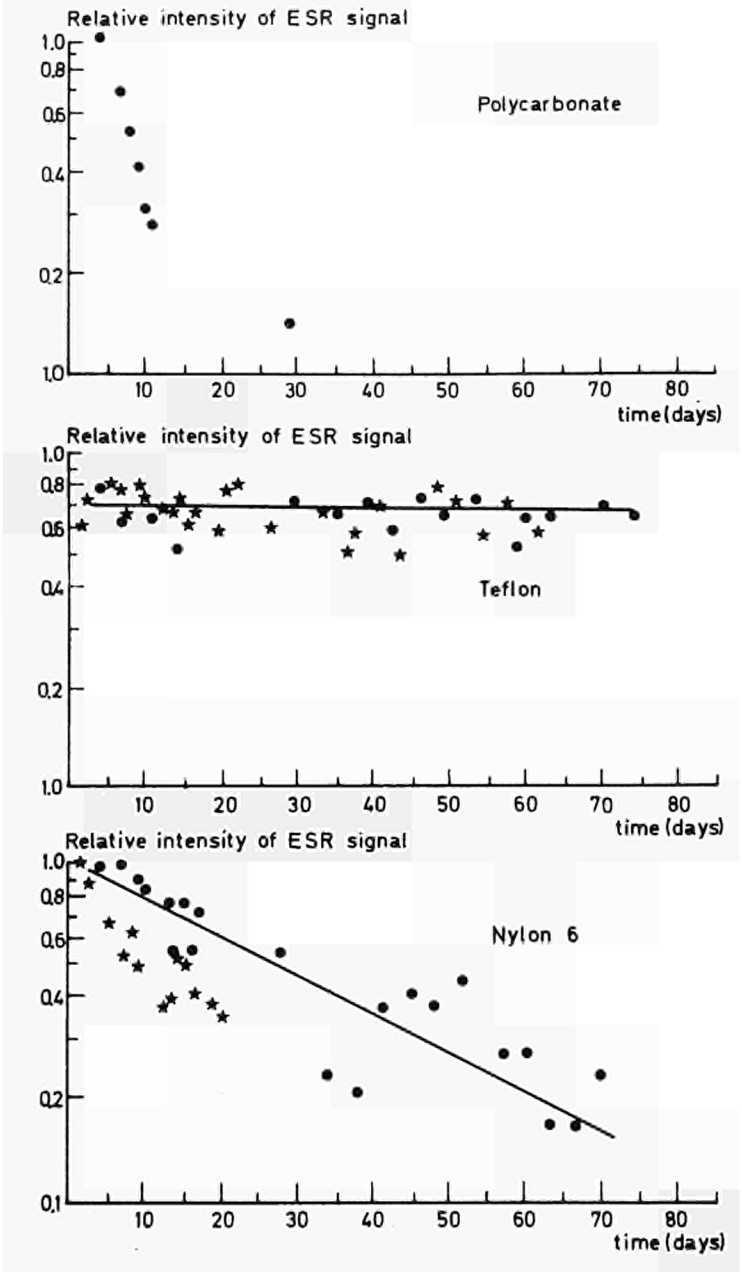

Relative intensity of ESR signal
Polycarbonate
Teflon
Nylon 6
time (days)

Fig. 7

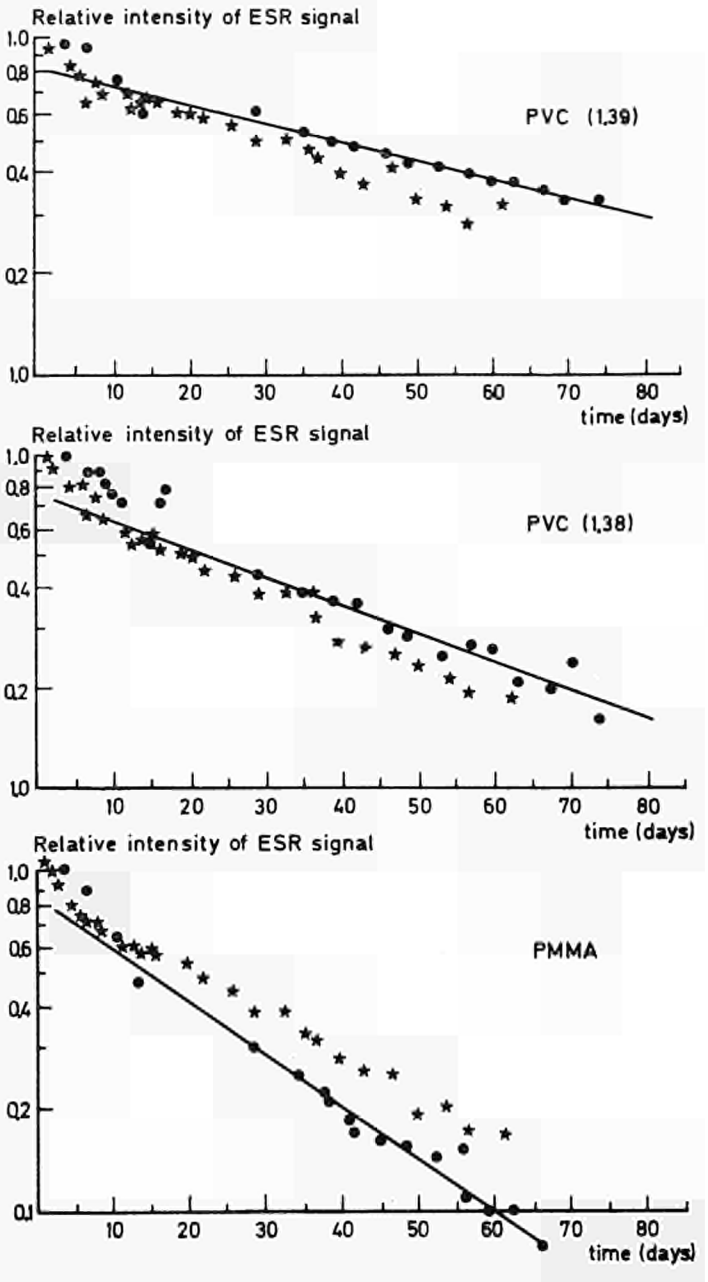

Relative intensity of ESR signal
PVC (1,39)
PVC (1,38)
PMMA
time (days)

Fig. 8

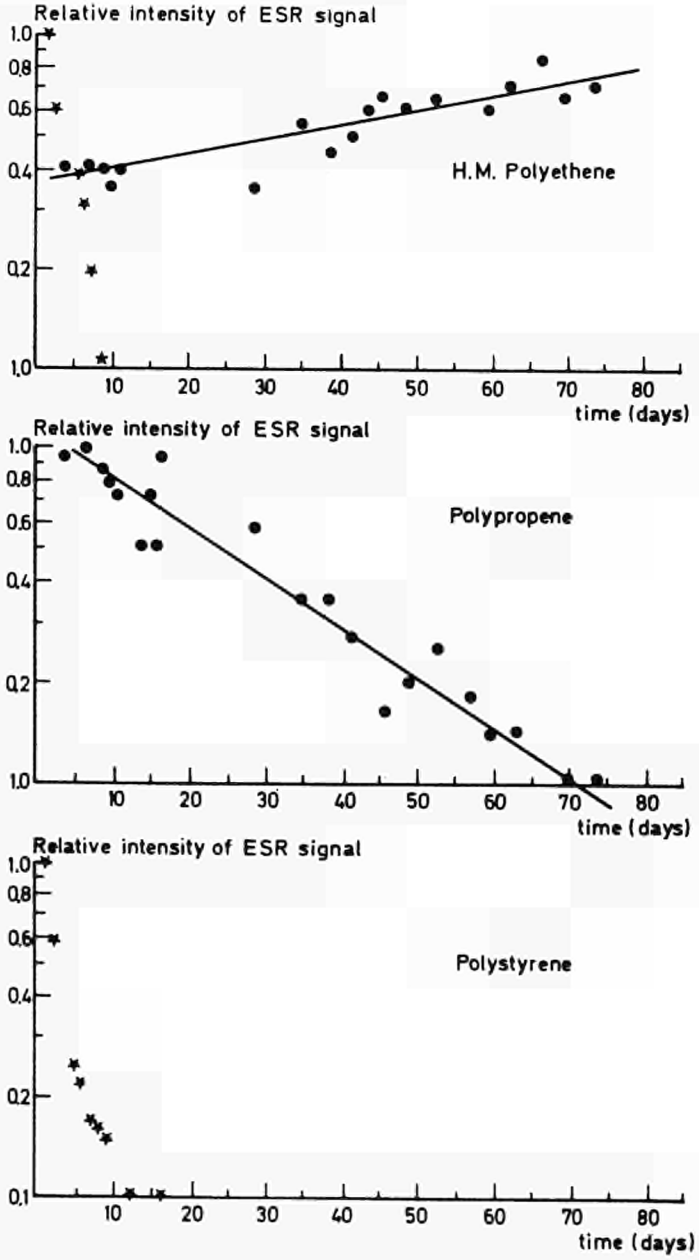
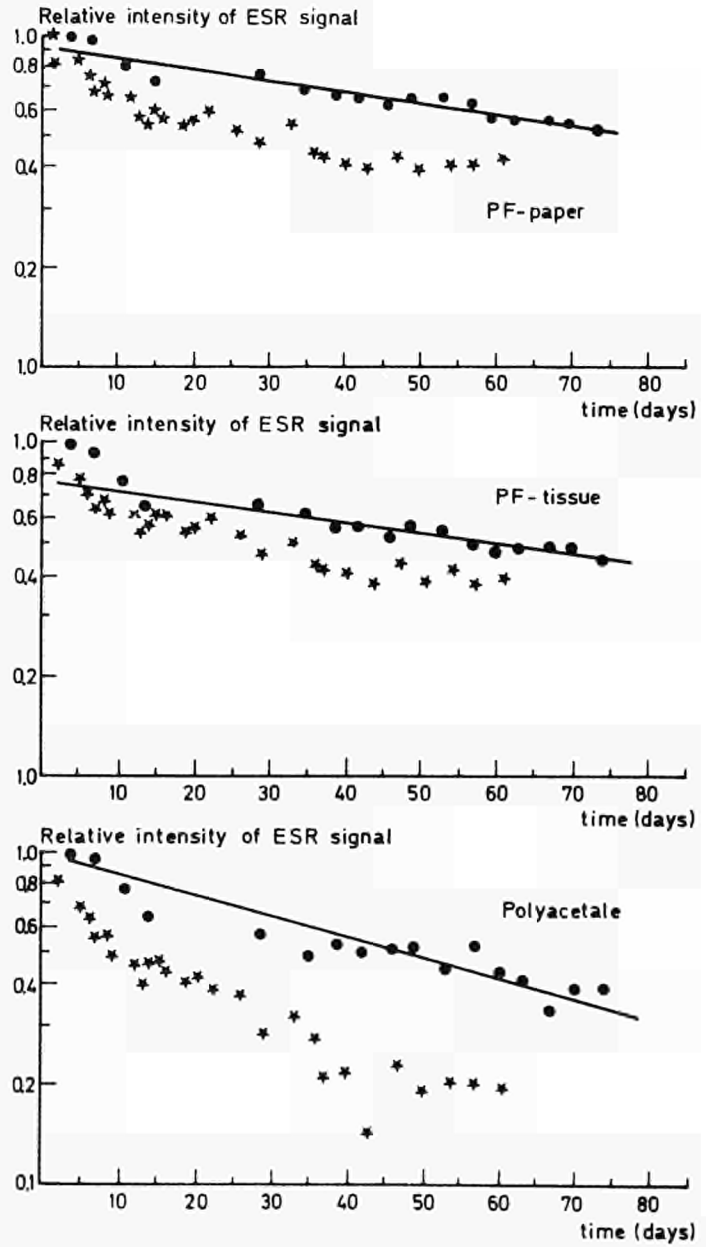


Fig. 9



Figs. 6, 7, 8 and 9 — The relative amplitude of the ESR signal in some polymers on a logarithmic scale versus time. The straight line shows exponential decrease for a fraction of the radicals.

* decay in an evacuated sample tube
● decay in an open sample tube (in air)

The irradiations were performed in evacuated tubes at room temperature to a dose of 2 Mrad. The dose rate was 0.66 Mrad/h for the samples which were to decay in vacuum and 0.13 Mrad/h for the other samples.

distinguishable, disappear exponentially upon irradiation. The dose at which half of the original radicals were destructed was found to be 6 Mrad. This corresponds to a value of the constant β of about 0.12 $Mrad^{-1}$, which is of the same order of magnitude as the value found for PVC in the present study.

In order to describe the saturation effect we introduce the following model that resembles in some respects a model put forward earlier by Ten Bosch[26]. This model is based on the fact that the energy of the secondary electrons liberated by the γ-radiation, is dissipated locally in isolated regions, which are called spurs[28].

It is assumed now that the radicals created in a spur are highly reactive and mobile during a certain time τ and can annihilate whit each other and with the already present immobile radicals. After the active period the initially formed radicals will be immobilized. Deposition of energy ΔW in the local volume V^* will lead to the creation of radicals. The concentration of these radicals as a function of the time t after the deposition of the energy is denoted by $n^*(t)$. The concentration of the existing immobile radicals is denoted similarly by $n(t)$. The radical destruction process in the volume V^* is then for $t < \tau$ described by

$$\frac{dn^*(t)}{dt} = -k_1 n^{*2}(t) - k_2 n^*(t)\, n(t)$$

$$\frac{dn(t)}{dt} = -k_2 n^*(t)\, n(t) \tag{2}$$

where k_1 and k_2 are the reaction rates.

It is assumed that the number of primary radicals formed locally is large compared to ultimately remaining immobile radicals. This assumption is equivalent to the assumption that the number of annihilation reactions occurring after the energy deposition is large. This implies $n^*(0) \gg n(0)$, so that for the $t = \tau$, the solution to the equations (2) is given by

$$n^*(\tau) = \frac{n^*(0)}{n^*(0) k_1 \tau + 1} \approx \frac{1}{k_1 \tau}. \tag{3}$$

$$n(\tau) \ll n^*(\tau).$$

It is to be noted that the number of radicals formed locally is constant and independent of the initially present radicals. Introducing the radical yield G_s of stable radicals in the local volume V^* equation (3) becomes

$$n^*(\tau) = G_s \Delta W / \rho V^* \tag{4}$$

Since at $t = \tau$, $n^*(\tau)$ becomes $n(0)$ again per definition, we may write the following differential equation for the mean concentration of stable radicals

$$\frac{dn}{dD} = G_s - \frac{\rho V^*}{\Delta W} n \tag{5}$$

where D denotes the absorbed dose.
Integration of equation (5) yields

$$n(D) = G_s \frac{\Delta W}{\rho V^*} \left(1 - \exp - \frac{\rho V^*}{\Delta W} D\right)$$

$$= n(\infty)\,(1 - \exp - \beta D). \tag{6}$$

From the value β we find for PVC $(\rho V^*/\Delta W) = 0.2$ $Mrad^{-1} = 3{,}2 \times 10^{-21}$ gram/eV. If V^* is identified with the volume of a spur, ΔW is about 100 eV, the energy that is deposited in

a spur[28]. For $\rho \approx 1$ a spur radius will be about 40 Å, a reasonable value as compared with values found in the literature. Kupperman[27] for instance uses in his calculation values of 30 Å. Since the weight of a polymer falls in the same order of magnitude as the weight value found for ρV^*, it is possible that the annihilation of the radicals in the volume V^* takes place via a chain of covalent bonds.

We assume that the temperature effect of the radical yield, as observed in PVC, is due to thermal decay of radicals. From measurements of the radical concentration as a function of the time after the irradiation (fig. 6) it appears that the decay follows first order kinetics. The temperature effect can be accounted for in equation (5) by introducing an additional term

$$\frac{dn}{dD} = G_s - \frac{\rho V^*}{\Delta W} n - \frac{\lambda_T n}{\dot{D}} \tag{7}$$

where λ_T is the temperature dependent rate constant for thermal decay and $\dot{D}$ the dose rate. Integration of eq (7) gives

$$n(D) = \frac{G_s}{\frac{\rho V^*}{\Delta W} + \frac{\lambda_T}{\dot{D}}} \cdot \left\{1 - \exp\left[-\left(\frac{\rho V^*}{\Delta W} + \frac{\lambda_T}{\dot{D}}\right) D\right]\right\} \tag{8}$$

Since the rate constant, λ_T, increases with increasing temperature, as described in the paragraph 3.3 it follows from the model proposed above, that at a higher temperature the number of radical induced by a given dose decreases. The initial slope of the $n(D)$ *vs* D curve should be independent of temperature.

Although the experimentally determined initial slopes at various temperatures did not confirm this conclusion, the deviation observed might well be due to the inaccuracy of the slope determination.

The measurements on PVC at doses higher than 1 Mrad, at 45 °C and at 60 °C, are qualitatively described by equation (8) for the dose rates 0.11 Mrad/h and 0.66 Mrad/ h(figs. 4 and 5). In contrast to the behaviour of the yield at higher temperatures a lower yield is found for a higher dose rate at room temperature. This effect can be described by a model which assumes overlap of volumina V^* during their active period. If two volumina V^* overlap during their active period the number of stable radicals after the active period will still be given by $G_s \Delta W$. The same statement holds for multiple overlap. We therefore put for the number of stable radicals created in a volume V^*

$$\sum_{j=0}^{\infty} K_j \frac{G_s \Delta W}{j+1} \tag{9}$$

where K_j the chance for j-fold overlap of the volumina considered. If the deposition of energy amounts ΔW is random, K_j has a Poisson distribution

$$K_j = \frac{1}{j!}\left(\frac{\dot{D}\rho V^* \tau}{\Delta W}\right)^j \exp -\left(\frac{\dot{D}\rho V^* \tau}{\Delta W}\right). \tag{10}$$

The resulting number of stable radicals, n_s, created in a volume V^*, can be written as

$$n_s = G_s \Delta W \frac{\Delta W}{\dot{D}\rho V^* \tau}\left\{1 - \exp -\frac{\dot{D}\rho V^* \tau}{\Delta W}\right\}. \tag{11}$$

The differential equation for the mean concentration of radicals can now be given as

$$\frac{dn}{dD} = \frac{G_s \Delta W - n\rho V^*}{\dot{D}\rho V^* \tau}\left(1 - \exp -\frac{\dot{D}\rho V^* \tau}{\Delta W}\right) - \frac{\lambda_T n}{\dot{D}}. \tag{12}$$

When the term $\lambda_T n$ is neglected the solution reads

$$n(D) = \frac{G_s \Delta W}{\rho V^*} \left\{ 1 - \exp\left[- \frac{D}{\dot{D}\tau} \left(1 - \exp - \frac{\dot{D}\rho V^* \tau}{\Delta W} \right) \right] \right\}. \tag{13}$$

For small doses it follows from equation (13) that the radical yield G is given by

$$G = G_s \frac{\Delta W}{\dot{D}\rho V^* \tau} \left(1 - \exp - \frac{\dot{D}\rho V^* \tau}{\Delta W} \right). \tag{14}$$

Inserting the initial radical yields of PVC at 0.11 Mrad/h ($= 6 \times 10^{16}$ 100 eV/gram.h) and 0.66 Mrad/h ($= 4 \times 10^{17}$ 100 eV/gram.h) in equation (14) leads to

$$G_s = 6 \text{ spins}/100 \text{ eV}$$

and

$$\frac{\rho V^* \tau}{\Delta W} = 1.2 \times 10^{-20} \text{ gram h/eV}.$$

The value of G_s thus calculated is nearly equal to the value found at room temperature and dose rate 0.11 Mrad/h.

With the value of $\rho V^*/\Delta W = 3 \times 10^{-21}$ gram/eV the active period τ is estimated to be 4 h.

Due to the inaccuracy of the measurements the uncertainty of this value is quite large and gives therefore only an indication of the order of magnitude.

However the estimated magnitude of τ is far too large to identify the active period as the life time of a spur. According to Mozumber[28] the time scale of the events in a spur is many orders of magnitude smaller. Chemical reactions that occur in spurs range over the time scale of 10^{-10} to 10^{-6} sec. Neutralization reactions of charged particles extend over several orders of magnitude in time. For non polar media of high viscosity the time scale is 10^{-6} - 10^{3} sec. Although times involved in the latter processes come closer to value of τ estimated here, they still seem too small to account for the observed dose rate effect. Therefore we believe that the active period of the radicals is not determined by a spur like effect. One can imagine that radicals are mobile in the solid material and that their mobility will only end because they are trapped somewhere. We suggest that the mobile radicals are actually observed directly after the irradiation as shown in figure 6 and that they are thus responsable for the observed fast decay process.

The observed decay in PVC and most of the other polymers is after a few days, best described by first order kinetics. It seems difficult to explain the decrease of the existing free radicals by the mechanism described above, that is by assuming free mobility in the sample coupled to an annihilation process in the encounter of two radicals. For in that case one would expect second order decay in contrast to the first order kinetics generally observed[29,30]. Explanations for the first order decay behaviour are:

a) combination of radicals with another radical trapped in close proximity,
b) the rate-determining step is the untrapping of the stable radicals, which then become free to diffuse and react with other radicals.

In polymers that are partly crystalline and partly amorphous the situation is more complex. Radicals formed in the crystallites will migrate and finally react within this amorphous region. This last step will be relatively fast above the glass temperature.

Another aspect of the decay is the influence of diffusing gases in the sample. These gases can be dissolved in the polymer during the irradiation or diffuse into the sample after the irradiation. The influence of diffusing gases in the sample is most clearly seen in polyethene, where the rate constant for decay in vacuum is 4×10^{-6} sec^{-1}, while in air the ESR signal is even found to increase. The same effect has been found by Abraham and Whiffen[6].

Finally another complicating aspect can be mentioned; the presence of impurities or chemical additions. If radicals move at random through the solid until each of them reaches a partner a large number of steps is involved. It can be imagined that during such a lengthy promenade the abovementioned impurities can intervene in the reaction by reacting with the perambulating radicals[31].

Considering all these effects in conjunction with the experimental results available a detailed evaluation of the decay curves seems not to be appropriate therefore at this moment.

5 — CONCLUSION

From the present study on the induction of free radicals in polymers that can be used as packaging material it follows that for most cases the radicals can be measured during a period of the order of 2 months after irradiaion with a dose of a few Mrad. Exceptions are formed for polymers with a large fraction in the glass state above the glass temperature and for polymers with plasticizers. The number of radicals created in the polymers was found to depend on irradiation conditions such as dose rate, temperature and gas environment. A model which accounts qualitatively for some of these parameters is given. Decay times were also found to depend on these parameters. It is therefore not possible to deduce accurately from an ESR measurement to what dose a sample is irradiated, even if the date of any possible irradiation can be estimated. An exception is formed by Teflon, where at room temperature no decay of any significance could be observed.

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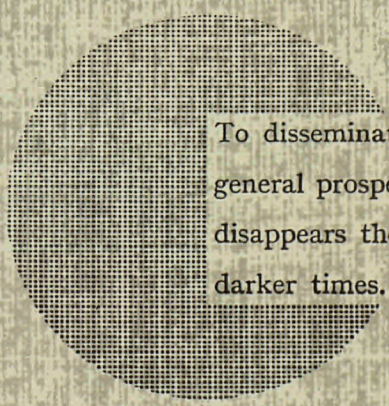

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